

Non-Ideal Behavior in Solvent Extraction

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SUMMARY

This report presents a summary of the work performed to meet FCR&D level 3 milestone M31SW050801, "Complete the year-end report summarizing FY11 experimental and modeling activities." This work was carried out under the auspices of the Non-Ideality in Solvent Extraction Systems FCR&D work package. The report summarizes our initial considerations of potential influences that non-ideal chemistry may impose on computational prediction of outcomes in solvent extraction systems. The report is packaged into three separate test cases where a robustness of the prediction by SXFIT program is under scrutiny. The computational exercises presented here emphasize the importance of accurate representation of both aqueous and organic mixtures when modeling liquid-liquid distribution systems. Case #1 demonstrates that non-ideal behavior of HDEHP in aliphatic diluents, such as *n*-dodecane, interferes with the computation. Cases #2 and #3 focus on the chemical complexity of aqueous electrolyte mixtures. Both exercises stress the need for an improved thermodynamic model of an aqueous environment present in the europium distribution experiments. Our efforts for year 2 of this project will focus on the improvements of aqueous and non-aqueous solution models using fundamental physical properties of mixtures acquired experimentally in our laboratories.

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ACRONYMS

AMUSE	Argonne Model for Universal Solvent Extraction
D	Distribution ratio
DTPA	Di 2-ethylenetriamine-N,N,N',N'',N'''-pentaacetic acid
FCR&D	Fuel Cycle Research and Development
HDEHP	Di(2-ethylhexyl) phosphoric acid
ICPMS	Inductively Coupled Plasma Mass Spectrometry
INL	Idaho National Laboratory
logK	Logarithm of an equilibrium constant
NIST	National Institute of Standards and Technology
SEPHIS	Solvent Extraction Process Having Interaction Solvents
SXFIT	Solvent eXtraction FITting computational package
TALSPEAK	Trivalent Actinide Lanthanide Separations by Phosphorus-reagent Extraction from Aqueous Komplexes

1. INTRODUCTION

For decades now the ability of using calculations to predict the behavior of chemical systems has driven the evolving field of scientific computing. The advantages of projecting chemistry on a computer screen are numerous, starting with efficiency of simulations and comfort of controllability. Since the advent of modern age computing every field of scientific inquiry progressively incorporated modeling into its research portfolio. In the area of hydrometallurgical recovery of valuable metals, where the separation is based on selective material distribution between two immiscible phases, i.e. solvent extraction, the capability of predicting the speciation of the metal ion in a liquid-liquid system remains the overarching goal. Such computational capability enables the tracking of mass balances in a distribution system, predicting, based on any given set of conditions, the final destination of metal ions, i.e. the outcome of the separation. This report summarizes the first year effort of a collaborative team of researchers assembled to illustrate how fundamental experimental inquiry blends with computational modeling to support separations based on liquid-liquid distribution. The backbone of the project is the computer program SXFIT [1], which, given sets of experimental data, identifies the probability of any user suggested equilibrium set guiding that specific separation. The furthestmost objective of this research endeavor is to identify obstacles, which obstruct an accurate computational prediction by SXFIT, thus affecting an overall confidence in its final answer. As such, the bulk of our experimental inquiry is concentrated on studying non-ideal chemistry in solutions on computational prediction. Complications arising from non-ideal behavior of solution components are certain when modeling chemical systems as complex as those utilized when recycling actinides from dissolved used nuclear fuel. Here, we present the “act one” of the project, where we illustrate how non-ideal solution behavior may interfere with the proper interpretations of solvent extraction data and computational predictions by SXFIT. We also introduce the concept of building thermodynamic models of solutions to allow quantitative description of chemical interactions in complex liquid phases. The construction of such thermodynamic models allows for numerical representation of non-ideal solute behavior in aqueous and organic phase components of a liquid-liquid distribution, and, when incorporated into SXFIT, a more accurate characterization of some liquid-liquid distribution equilibria.

A survey of computational modeling studies in the area of actinide recovery from dissolved used nuclear fuel outlines two distinct tactics when simulating separations. The first approach is a dynamic simulation of material balance across a series of unit operations. Here a developed simulation code such as SEPHIS, SOLVEX, AMUSE or PAREX predicts the distribution behavior of a solute in an engineered separation flowsheet of mixer-settlers or a multistage bank of centrifugal contactors. [2-5] The second approach is a steady-state calculation of final speciation in a two-phase system after the attainment of a thermodynamic equilibrium. It is an equilibrium-based approach where, based on the available experimental data, the distribution of a metal ion may be calculated using non-linear least squares regression to solve mass-balance equations. [6-8] The computational package SXFIT, together with its predecessor codes SXLSQ [9], SXLSQA [10], and SXLSQI [11], was built on an equilibrium-based platform, and offers a great number of advantages, which a simple least squares minimization routine cannot. SXFIT accepts sets of experimental data (distribution coefficients, absorbance data, osmotic coefficients, concentrations at equilibrium) and prompts the user to define a model (set of chemical reactions that occur in a mixture of identified components). Once defined the program uses the equilibrium constants, solute activity coefficients and solvent activities to calculate

concentrations of each system component at equilibrium. Further, once calculated the program refines the equilibrium constants to match the experimental data. SXFIT, supplied with required parameters, calculates the activity coefficients and osmotic coefficients for species present in aqueous electrolyte mixtures based on Pitzer ion interaction theory. [12] Regular solution theory is used to perform similar calculations for solutes and solvent in the organic phase. [13] As such the program offers an option to consider the effects of non-ideal solution chemistry when predicting sets of operating chemical reactions during separation process.

Our considerations of non-idealities in solvent extraction systems are packaged into three separate test cases where a robustness of the SXFIT prediction is under scrutiny:

- 1) Modeling of the Diluent Effect for the Extraction of Trivalent Metals by Dialkyl Phosphoric Acid from Mineral Acid Solutions.
- 2) Effect of Preliminary Thermodynamic Model of Aqueous Malonate Buffer ($\text{Eu}^{3+} / \text{H}^+ / \text{Na}^+ / \text{NO}_3^- / \text{H}_2\text{Mal} / \text{HMal}^- / \text{H}_2\text{O}$) on SXFIT Prediction for the Extraction of Trivalent Metals by Dialkyl Phosphoric Acid from Malonate Buffer Solutions.
- 3) Comparison of Independent SXFIT Predictions for the Same Liquid-Liquid Distribution System.

Case #1 will illustrate an example of a liquid-liquid distribution system where non-ideal behavior observed for the metal ion coordination reagent in an aliphatic diluent complicates the calculation by SXFIT program. This case clearly reiterates the importance of thorough thermodynamic characterization of the system. Case #2 summarizes the earliest examination of the effects of an assembled thermodynamic model of the investigated aqueous electrolyte mixture on the SXFIT prediction. This exercise yields a direct indication of the effects of non-idealities on modeling solvent extraction systems. Case #3 explores computational robustness of the program.

2. APPROACH

In this report series of distribution ratios were collected at various conditions to prepare an experimental database as part of the input file for predictive modeling exercises using the SXFIT program. Metal extraction was quantified by the distribution ratio, D , calculated as the ratio of the equilibrium concentration of the metal ion in the organic phase to that in aqueous phase. The organic solutions of the extractant were pre-equilibrated with equal volumes of aqueous electrolyte solutions immediately prior to use. An aliquot of the pre-equilibrated organic phase was then contacted with an equal volume of the identical aqueous phase spiked with radiotracers. The two phases were vigorously shaken for at least 2 hours (overnight for TALSPEAK-related conditions) at room temperature, 20 ± 2 °C. The samples were centrifuged to facilitate phase separation and an aliquot of each phase was taken for either radiometric measurements using gamma spectrometry or ICPMS analysis. Aqueous malonate buffers were prepared using standard lanthanide stock solutions characterized using ICPMS, oven dried malonic acid, ultrapure sodium nitrate and HPLC-grade water. The pH adjustment was followed with a Ross semimicro glass combination electrode. The electrode was calibrated to an operational $\text{p}[\text{H}^+]$ scale ($\text{p}[\text{H}] = -\log [\text{H}^+]$, where $[\text{H}^+]$ is the molar hydrogen ion concentration in solution) through

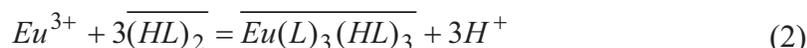
a Gran titration of HNO₃ with NaOH at 0.5 M ionic strength adjusted with NaNO₃ prior to pH adjustment. Under these conditions, the measured p[H⁺] was accurate to ± 0.005 p[H⁺] units.

The reader is referred to the FCR&D report [14] for a detailed description of the SXFIT computational package.

3. SUMMARY OF RESULTS

Case #1: *Modeling of the Diluent Effect for the Extraction of Trivalent Metals by Dialkyl Phosphoric Acid from Mineral Acid Solutions.*

The liquid-liquid distribution of trivalent europium between aqueous mineral acid solutions and non-aqueous solutions of an organophosphorous phase transfer reagent was subjected to SXFIT modeling routine. The phase transfer reagent – di(2-ethylhexyl)phosphoric acid (HDEHP) – was diluted either in an aromatic solvent, toluene, or an aliphatic solvent, *n*-dodecane. As such two experimental datasets were produced where the distribution of Eu³⁺ was monitored as a function of the progressively increasing concentration of HDEHP (Figure 1). When aqueous acidic solutions containing trivalent metal ions are contacted with the organic mixtures of HDEHP the hydration sphere of the metal is replaced by coordinating donor groups of HDEHP. This reaction occurs at the aqueous/organic interface, where the metal is coordinated by three HDEHP dimers; it crosses the phase boundary and enters the organic environment. The equilibrium set that governs this process may be described by equations 1 and 2,



where HL is HDEHP and the horizontal bar represents species in the non-aqueous phase [15]. Equilibrium 1 describes the dimerization of HDEHP in non-polar diluent. Equilibrium 2 is a phase transfer reaction.

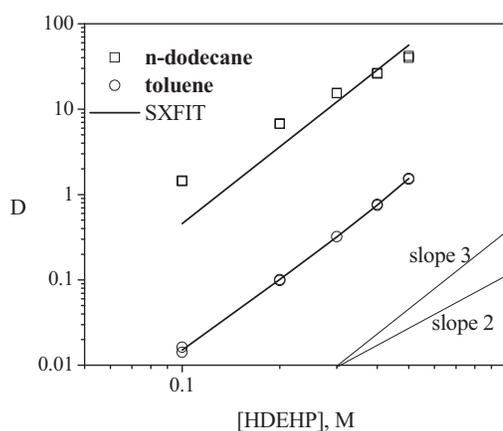


Figure 1. Experimental and SXFIT-calculated distribution ratios for Eu³⁺ extraction from mineral acid solutions by HDEHP dissolved in *n*-dodecane and toluene.

SXFIT reproduces the experimental datasets by adjusting the equilibrium constants of user specified chemical reactions responsible for liquid-liquid distribution, and calculating the

concentration of each species in either phase at equilibrium, i.e. a distribution ratio, D . Distribution ratios calculated by SXFIT for the equilibrium set described by equations 1 and 2 are shown in Figure 1 using continuous lines to emphasize the goodness of fit.

For the toluene system SXFIT reproduces the experimental distribution ratios very well, yielding a $\log K = 1.137 \pm 0.013$ for the equilibrium 2. The agreement is much poorer for the dodecane system. Using the same equilibrium set (eq. 1,2) SXFIT is unable to reproduce D values. In fact SXFIT calculation produced multiple answers when other equilibrium sets were suggested. Both, liquid-liquid distribution by a monomeric and trimeric HDEHP represent the dodecane dataset very well. Such an anomaly introduces an element of caution into the interpretation of the SXFIT calculations and reiterates the importance of thorough thermodynamic characterization of the system. The most feasible explanation for the observed mismatch between the experiment and the calculation may stem from the substantial non-ideal behavior of HDEHP in the non-polar environment of n -dodecane. Vapor pressure osmometric measurements are currently in progress to delineate the influence of solute-solute interactions on the distribution of europium in this system. Such experimental thermodynamic inquiry will further develop the understanding of the solution chemistry, which, in turn, will allow reliable SXFIT prediction.

Case #2: Effect of Preliminary Thermodynamic Model of Aqueous Malonate Buffer ($\text{Eu}^{3+} / \text{H}^+ / \text{Na}^+ / \text{NO}_3^- / \text{H}_2\text{Mal} / \text{HMal}^- / \text{H}_2\text{O}$) on SXFIT Prediction for the Extraction of Trivalent Metal by Dialkyl Phosphoric Acid from Malonate Buffer Solutions.

Accurate characterization of some liquid-liquid distribution equilibria relies on proper consideration of non-ideal solution chemistry in aqueous electrolyte and non-aqueous solute mixtures. Quantitative description of chemical interactions in complex liquid phases may be realized through the process of thermodynamic parameterization of theoretically represented mixtures. The construction of such thermodynamic models allows for numerical representation of non-ideal solute behavior in aqueous and organic phase components of a liquid-liquid distribution. To provide an initial glimpse of how such thermodynamic representation might impose on SXFIT prediction a preliminary thermodynamic model for the aqueous buffer: $\text{Eu}^{3+} / \text{H}^+ / \text{Na}^+ / \text{NO}_3^- / \text{H}_2\text{Mal} / \text{HMal}^- / \text{H}_2\text{O}$, where Mal describes malonate, was constructed based on Pitzer ion-interaction theory. A thorough experimental database of europium distribution ratios was collected using conditions relevant to the constructed thermodynamic model. Europium distribution between aqueous malonate buffer mixtures of varying acidity and total malonate content and organic dilute mixtures of HDEHP in n -dodecane was studied to assemble the SXFIT experimental input data.

The aqueous conditions chosen for this study sought to maintain consistency with the common aqueous conditions present in the TALSPEAK process – a solvent extraction method designed to separate trivalent actinides from trivalent lanthanides in treatment of used nuclear fuel effluents. [16] In TALSPEAK a well balanced thermodynamic competition for metal ion coordination by an aqueous aminopolycarboxylate reagent, DTPA, and non-aqueous organophosphorus phase transfer reagent, HDEHP, affords the separation of the two chemically similar f -element families. The traditional TALSPEAK aqueous phase consists of up to 2 M lactate buffer, which assists in several process-related facets such as kinetics, phase disengagement, and reagent solubility. [16,17] Lactate, however, is a renowned culprit in

TALSPEAK-type separations due to its tendency to enter the organic phase, thus rendering any modelling attempts of lactate-containing liquid-liquid systems a dreadful task. [18] To circumvent lactate's problematic properties we replaced it with malonate in TALSPEAK solutions. Figure 2 compares the distribution of lanthanides (La^{3+} - Ho^{3+}) and americium between lactate and malonate solutions containing 50 mM DTPA and 0.1 M HDEHP in *n*-dodecane. The distribution ratios practically overlap illustrating the validity of malonate-for-lactate swap.

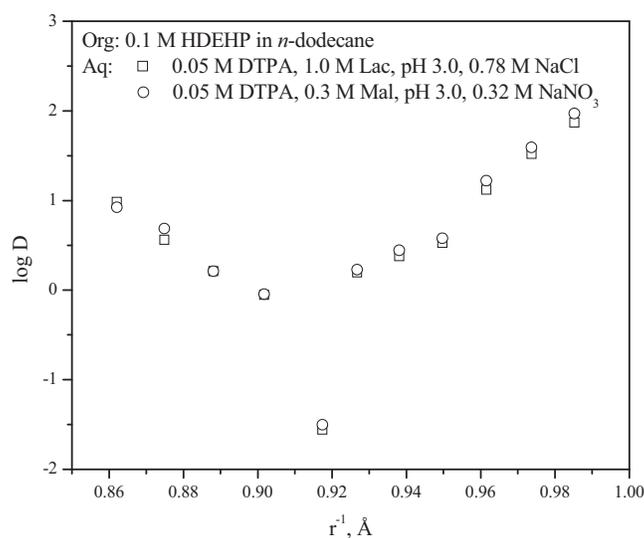


Figure 2. Comparison of the distribution of lanthanides (La^{3+} - Ho^{3+}) and americium between aqueous lactate and malonate solutions containing 50 mM DTPA and organic solution of 0.1 M HDEHP in *n*-dodecane. Total lanthanide concentration was 1 mM.

To construct the preliminary thermodynamic model without the presence of DTPA in solution the following initial composition of an aqueous mixture was assumed, where the concentrations are reported in molalities, m , i.e. mole of solute per kg of solvent.

$$m\text{Na}^+ = 0.566, m\text{Eu}^{3+} = 0.001, m\text{NO}_3^- = 0.349, m\text{OH}^- = 0.22, m\text{H}_2\text{Mal} = 0.3$$

The presence of OH^- in the initial conditions is warranted to yield a calculated pH of approximately 3.0. The thermodynamic model was built using an extended form of the Pitzer ion-interaction model for estimating water activities and osmotic coefficients in aqueous electrolyte mixtures. [19] Table 1 summarizes the initial parameters for the Pitzer model generated for the $\text{Eu}^{3+} / \text{H}^+ / \text{Na}^+ / \text{NO}_3^- / \text{H}_2\text{Mal} / \text{HMal}^- / \text{H}_2\text{O}$ aqueous buffer. It is important here to indicate that this model has been constructed on the basis of available literature data for mixtures related to our conditions. In many cases the quality of this literature data is unknown and on most occasions scarce. As such some elements of the model need to be treated with caution. While building the model the sensitivity analyses identified ion interactions of significant importance to accurate representation of this electrolyte mixture. Some of those interactions (Eu^{3+} - HMal^- , Eu^{3+} - Na^+ - NO_3^-) are currently being studied experimentally in our laboratory using isopiestic equilibration, solvent extraction, spectrophotometry, and potentiometry. Those experiments are ongoing, and once data collection is completed the results will be represented using Pitzer ion interaction theory to revise the current model.

Table 1. Summary of the Pitzer parameters for the preliminary thermodynamic model for the aqueous malonate buffer solutions used in this study.

Interaction	β_0	β_1	C_ϕ
$H^+-NO_3^-$	0.11190	0.36860	0.002470
$Na^+-NO_3^-$	0.006800	0.1783	-0.000720
Na^+-HMal^-	0.0387	0.1777	-0.002949
Na^+-Mal^{2-}	0.2058	1.3243	-0.013910
$Eu^{3+}-NO_3^-$	0.4755	5.1333	-0.048382
$Eu^{3+}-HMal^-$	0.4755	5.1333	-0.048382
$Eu^{3+}-Mal^{2-}$	0	0	0
H^+-Mal^{2-}	-0.0084	0.3147	0.028828
H^+-HMal^-	0.2959	0.4005	-0.011316

The organic conditions for this study required dilute concentrations of a phase transfer reagent HDEHP to determine quantifiable distribution ratios for europium. Such a dilute presence of HDEHP was advantageous to our investigations in that the complication due to non-ideal behavior of extractant dimers in the aliphatic diluent was negligible. For the SXFIT modeling purposes an ideal behavior of HDEHP in solution was assumed.

Figure 3a shows the collection of liquid-liquid distribution dependencies for the europium extraction by five different concentrations of HDEHP in *n*-dodecane from malonate media of varying total amounts have been completed, keeping the concentration of bimalonate constant, and varying the $p[H^+]$ from 1.8 to 2.5. These distribution dependencies were modeled using SXFIT. When the raw europium distribution ratios are plotted as a function of aqueous acidity a slope of -2.0 for this dependency was observed. A slope of -3 would be expected for this well known mechanism of extraction of a trivalent metal ion by the liquid cation exchanger. It is important to recognize that the extraction of europium by HDEHP counters an aqueous complexing influence of malonate species. As such a correction for this holding-back contribution from malonate is of value during a graphical analysis of this distribution data. When the raw distribution ratios were corrected using equation 3 (concentration of bimalonate was constant) the slopes of acid dependencies increased to a collective average of -2.7. The values for the binding constants were found in NIST database, collected at the 0.5 M ionic strength. [20] The observed deviation from -3 slope could be due to some medium effects and accurate operation of the glass electrode in regions of highest acidity ($pH = 1.8$), where approximately 1.5 M total malonate is required to maintain the constant concentration of bimalonate at 0.2 M.

$$D^o = D(1 + \beta_{101}[Mal^{2-}] + \beta_{102}[Mal^{2-}]^2) \quad (3)$$

When the data is analyzed as a function of HDEHP concentration the expected slope of 3.0 is evident for 1 – 7.5 mM HDEHP concentration range. Figure 3b illustrates this for data collected at pH of 2.5. The last point of this dependency, corresponding to 10 mM, deviates from the expected value. This is most likely due to the onset of the non-ideal dimer interactions in the organic phase.

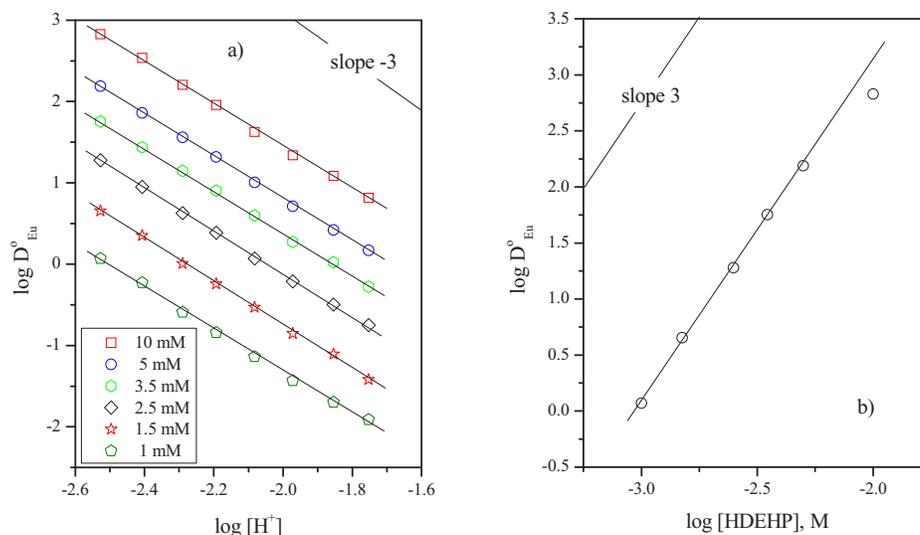


Figure 3. (a) Liquid-liquid distribution dependencies for the europium (5 μM) extraction by five different concentrations of HDEHP in *n*-dodecane from malonate media. Total malonate concentration was varied to maintain constant concentration of bimalonate at 0.2 M, while varying $\text{p}[\text{H}^+]$ from 1.8 to 2.5. Total anion concentration, $[\text{HMal}^-] + [\text{NO}_3^-]$, was 0.5 M. (b) Extractant dependency for the extraction of europium from a $\text{p}[\text{H}^+] = 2.5$ malonate buffer by HDEHP in *n*-dodecane.

Table 2. Summary of the SXFIT-refined equilibrium constants for the modeled liquid-liquid distribution of europium between aqueous malonate buffers and organic HDEHP in *n*-dodecane mixtures.

Equilibrium	LogK(Pitzer)	LogK(ideal)
$\text{Eu}^{3+} + 3\overline{(\text{HL})}_2 = \overline{\text{Eu}(\text{L})}_3\overline{(\text{HL})}_3 + 3\text{H}^+$	6.5	4.2
$\text{Na}^+ + \overline{(\text{HL})}_2 = \overline{\text{Na}(\text{L})(\text{HL})} + \text{H}^+$	-1.4	-2.3
Agreement factor	4.15	4.09

The results of the SXFIT calculations for the distribution of europium between aqueous malonate buffer solutions and organic mixtures of HDEHP in *n*-dodecane are presented in figure 4a. The model used to represent the experimental results may be described by equations 1, 2 and 4, where the extraction of europium and sodium by HDEHP occurs, respectively.



Table 2 compares the values of equilibrium constants for the reactions included in the model produced by SXFIT, when the refinement calculations assumed ideality in both phases with those obtained when initial Pitzer model was included. The listed agreement factors, i.e. goodness of fit, where 1 represents perfect fit, indicate a fair convergence between the experimentally gathered data and the values calculated by the program. The model struggles with

accurate interpretation of the distribution ratio set collected using 10 mM HDEHP in *n*-dodecane, reinforcing the complication arising from non-ideal behavior of HDEHP in the aliphatic diluent. The program reproduces the experimental distribution values very well for the datasets obtained using lower concentrations of the extractant.

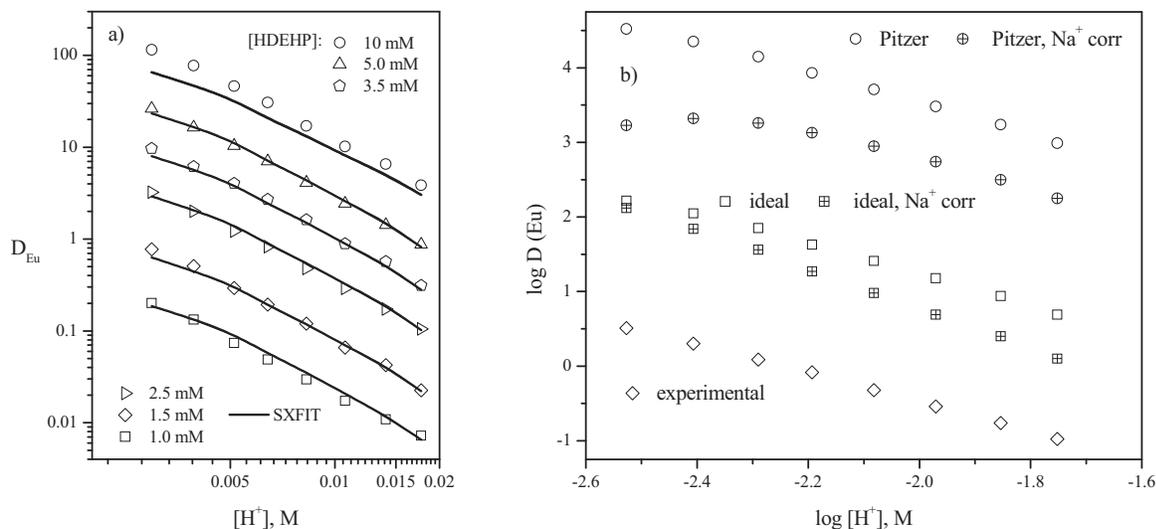


Figure 4. (a) Best fit results of the SXFIT minimization of all datasets on the europium distribution between aqueous malonate buffers and organic HDEHP/dodecane mixtures. (b) Comparison between the distribution ratios calculated using the equilibrium models predicted by SXFIT and the experimentally collected dataset for the acid dependency (pH 2.5 – 1.8) for the extraction of 5 μ M europium by 2.5 mM HDEHP in *n*-dodecane.

The most important observation to this investigation, however, is the influence of the incorporated Pitzer model on the SXFIT calculation. Comparing the refined equilibrium constants the effect appears important. When the non-ideal chemistry in the aqueous phase was considered in SXFIT calculations the europium extraction constant increased more than 2 orders of magnitude. This is very important from a predictive modeling perspective.

Using the equation 5 as the expression for the equilibrium constant for the extraction of europium in this system we may calculate the distribution of the metal ion using the equilibrium constants predicted by SXFIT.

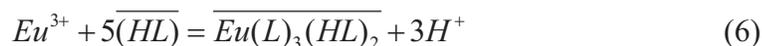
$$K_{ex} = \frac{[Eu(LHL)_3]}{[Eu^{3+}](1 + \beta_1[Mal^{2-}] + \beta_2[Mal^{2-}]^2)} \frac{[H^+]^3}{[HL]_{dim}^3} = D^o \frac{[H^+]^3}{[HL]_{dim}^3} \quad (5)$$

Figure 4b compares the predicted distribution ratios for the acid dependency (pH 2.5 – 1.8) for the extraction of 5 μ M europium by 2.5 mM HDEHP in *n*-dodecane, with those obtained experimentally. The distribution ratios were calculated with and without the consideration of the impact of sodium extraction on europium phase transfer. Additive extraction behavior was assumed when correcting for sodium co-extraction by calculating the effective concentration of the HDEHP dimer available for the europium extraction. The predicted distribution values are severely overestimated, both when ideality was assumed and our preliminary Pitzer model was incorporated into the calculation. Several factors may contribute to the great mismatch between

the calculated and the experimental data, which, in this early stage of our construction of the thermodynamic model, should not be alarming. The accuracy of the Pitzer model and its proper treatment of europium-malonate complexation have to be treated tentatively at this stage of our thermodynamic modeling effort. Even though the prediction using the Pitzer model appears inferior this particular calculation is expected to improve as more accurate theoretical representation of malonate mixtures are constructed. In the case where ideal behavior was assumed no further improvement is possible, and the mismatch illustrates (assuming SXFIT calculation was accurate) the importance of non-ideal behavior in predicting liquid-liquid distribution systems.

Case #3: Comparison of Independent SXFIT Predictions for the Same Liquid-Liquid Distribution System.

The SXFIT computational prediction relies on a user to specify the operational model, i.e. a system of equilibrium equations that guide the chemical reactions for any given system. As such the calculation may generate a number of answers depending on the user's initial guess. A better understanding of the chemistry in any liquid-liquid system under the investigation imposes rigorous constraints on a calculation in that only a single answer may represent a dataset accurately. To investigate such predictive ambiguities the data on the extraction of europium from malonate media by HDEHP in *n*-dodecane presented in the #2 case study was modeled independently by 2 scientists with working knowledge of SXFIT program. The purpose of this exercise was not to enter an argument on the validity of any proposed model. Rather it was an assessment of the tolerance limits for a non-linear least squares fitting routine constricted by a provided set of experimental data and a preliminary Pitzer model for aqueous malonate buffer. Figure 5 compares the best fit results for those two independent minimizations overlaid on the actual experimental data. This particular set of distribution ratios represented the extraction of europium from a $p[H^+] = 2.0$ malonate buffer using different concentrations of HDEHP in *n*-dodecane. Model I was presented as part of the case #2 study, where a Pitzer treatment for aqueous electrolyte buffer was included. Model II, together with the equation 1 for the dimerization of HDEHP, included the equilibrium described by equation 6.



The refined extraction constant for equation 6 was 4.2, with the agreement factor at 4.68 for the minimization. This modeling exercise demonstrates a message that has been repeated throughout our investigations. SXFIT program was able to reproduce the experimental data using two different equilibrium models to very similar goodness of fit, i.e. agreement factor. The existence of such ambiguity in a final answer points to inaccurate knowledge of chemical reactions (equilibria) and/or interactions (non-ideality) in the investigated system. As such further experimental inquiry is necessary and is currently in progress. We anticipate that the

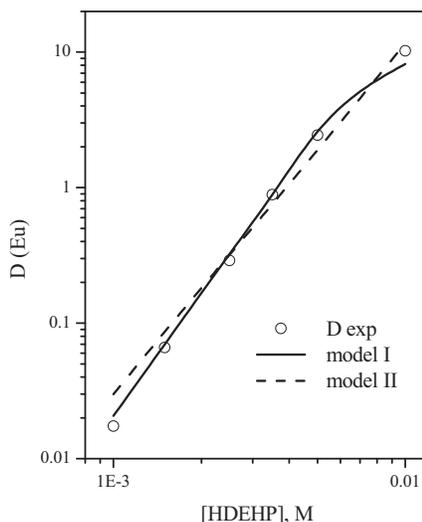


Figure 5. Comparison of independent SXFIT modeling evaluations for the selected set of distribution ratios representing the extraction of europium from a $p[H^+] = 2.0$ malonate buffer by different concentrations of HDEHP in *n*-dodecane. (\circ) experiment (—) model I (----) model II.

addition of our isopiestic data, together with other ionic strength dependencies of key complexation equilibria in this system, will improve the accuracy of the Pitzer model, constrain the minimization routine and eliminate the computational pitfalls illustrated here.

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5. MILESTONE PARTICIPANTS

1. Peter R. Zalupski, Idaho National Laboratory, PI
2. Laetitia Delmau, Oak Ridge National Laboratory, co-PI
3. Tatiana Levitskaia, Pacific Northwest National Laboratory, co-PI
4. Mikael Nilsson, University of California at Irvine, co-PI

6. INDICATORS OF PROJECT QUALITY

Peter Zalupski (INL), Michael Gray, Mikael Nilsson (Univ of California, Irvine), Laetitia Delmau (ORNL) “Using SXFIT to Model Liquid-Liquid Distribution Systems: Initial Results for the Extraction of a Trivalent Metal by Dialkyl Phosphoric Acid”, 2011 American Nuclear Society Annual Meeting Hollywood, Florida, June 26 – 30, 2011

GJ Lumetta, TG Levitskaia, JC Braley, JC Carter, AV Gelis, “TRUESPEAK Progress Towards Fundamental Understanding and Practical Applications,” 35th Annual Actinide Separations Conference, Charlotte, NC on May 25, 2011.

MF Gray, M Nilsson, PR Zalupski, “Characterizing the self-association and activities of di(2-ethylhexyl) phosphoric acid in n-dodecane using vapor pressure osmometry, 241st American Chemical Society, Anaheim, CA, March 27-31, 2011.

7. SUMMARY OF COLLABORATORS EFFORTS IN FY11

This project combines efforts of a unique blend of scientists who develop means for collection, evaluation and theoretical representation of solution mixtures partaking in aqueous partitioning processes considered for used nuclear fuel recycling. Dr. Laetitia Delmau (ORNL) has focused her efforts mainly on SXFIT predictive modeling of the collected experimental data at INL. A variety of liquid-liquid distribution data, which revolved around liquid-cation exchanging mechanism of extraction, has been collected and analyzed in FY11. Only some modeling results have been made part of this report to produce a concise informative package whose theme was the assessment of predictive validity of SXFIT computational program. Complete modeling report is available in the FCR&D report: Delmau, L.H. *Modeling distribution ratios and osmotic coefficients using SXFIT*, Fuel Cycle Research and Development Report, FCRD-SWF-2011-000320, August 2011.

Dr. Tatiana Levitskaia (PNNL) produced a tremendous body of experimental work in FY11 focusing on three overarching goals:

- Developing the methodology for determination of activity effects in aqueous electrolyte solutions.
- Assessing speciation phenomena in the aqueous and organic solutions applicable to the model TALSPEAK extraction process.
- Thermodynamic modeling of the metal ion extraction in the TALSPEAK and TRUSPEAK processes using SLXSQI software.

To study thermodynamic properties of aqueous electrolyte mixtures the Water Activity Meter was procured, calibrated and tested using NaCl, Nd(NO₃)₃, and LaCl₃ solutions in wide concentration range. The measured water activity values agreed well with the corresponding literature values for both 1:1 and 3:1 electrolyte systems. It was demonstrated that the Vapor Pressure Osmometry (VPO) method can be used to study water activity of the electrolyte solutions at low concentrations. The Pitzer parameters obtained for NaCl by the least squares fitting of the water activity data agreed well with the corresponding literature values, validating the overall methodology. OLI simulation was used to obtain the osmotic coefficients for lactic

acid, which are not reported in the open literature. It was concluded that OLI software can be further used to generate water activity and/or osmotic coefficient data for the electrolyte systems for which multiple physicochemical parameters are available but non-ideality effects have not been quantified.

To accurately represent any given 2-phase partitioning system the understanding of the speciation in each liquid phase is important. Such information allows the SXFIT user to supply an educated initial guess when suggesting an equilibrium model in an input file. The speciation phenomena in the metal-loaded TALSPEAK organic solvent and in the aqueous contact phases were investigated. For the organic phase speciation, the conducted studies were focused on the determination of HDEHP aggregation in an alkane solvent as a function of the composition of the contacted aqueous phases. It was determined that degree of loading of the organic phase with monovalent (Na^+) and trivalent (lanthanide Ln^{3+}) ions has the pronounced effect on the HDEHP aggregation and, therefore, transport of other components of the extraction system (e.g., lactate and H_2O) into the organic phase. For the aqueous phase, characterization of the ionization behavior of lactic acid at variable ionic strength and temperature has been initiated. In these tests, the dependence of lactic acid pK_a on temperature (25 to 55 °C) at ionic strength of 0.25 to 2 M was evaluated.

When modeling TRUESPEAK-related distribution data the newly acquired speciation/aggregation data and the Pitzer parameters for lactic acid were used. Equilibrium extraction constants corresponding to the formation of the $\text{NaA}(\text{HA})_3$ (low organic loading), $\text{NdA}_3(\text{HA})_2$ (low organic loading), and $\text{NdA}_3(\text{HA})$ (moderate organic loading) were obtained via SXLSQI fitting of the extraction data. The calculated Nd^{3+} extraction constants corresponding to the low and moderate loading regimes are in excellent agreement. The extraction constants for the mixed lanthanide-HDEHP-CMPO organic products suggest that addition of the neutral CMPO extractant to the HDEHP solvent has different effect on Nd^{3+} and Eu^{3+} extraction profiles, with the former exhibiting greater affinity to CMPO.

Complete research report is available in the FCR&D report: Levitskaia, T. *Non-Ideality in Solvent Extraction Systems: PNNL FY11 Status Report*, Fuel Cycle Research and Development Report, FCRD-SWF-2011-000302, August 2011.

Quantitative description of chemical interactions in complex non-aqueous mixtures is an overall objective of the research guided by Prof. Mikael Nilsson (UCI). Experimental inquiry into mixtures of HDEHP and *n*-dodecane continued in FY11 using vapor pressure osmometry. The most important accomplishment in this area of the project centers on the theoretical representation of the acquired data. The comparison between the calculated activity coefficients for HDEHP / *n*-dodecane solution with those predicted using solubility parameters revealed that Scatchard-Hildebrand theory is inadequate to accurately describe the system. As such a survey of other models is ongoing with an intent to identify or construct theory that would allow numerical representation of non-ideal solute behavior in such non-aqueous environments. If successful the identify theory will have to replace regular solution theory in the SXFIT code.